17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 The effective date of this SOP is the date in the header or last signature date, whichever is most recent.

17.6 Logbooks must be reviewed monthly by the department supervisor.

17.7 Logbooks must be reviewed quarterly by the QA Staff.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Initial Demonstration of Proficiency- Each analyst must perform an initial demonstration of proficiency on a method and matrix basis with a successful analysis of four LCS where acceptable precision and accuracy are generated. The accuracy component must fall within LCS criteria. The precision component must be less than 20% for duplicate RPD data.

19.2 Method Detection Limits (MDLs) must be determined on an annual basis (at minimum) or whenever major modifications are performed.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R04	8/1/12	CES	Formatting
R04	8/1/12	AK	Updating
R05	4/30/14	CES	Formatting; Update spike info and include audit response items.
R06	10/1/14	CES	Addition of sample screening procedure (sec. 12.1.5)
R07	8/3/15	CES	Addition of SIM analysis (sec. 21.10)

21) References and Related Documents

21.1 VOC Gases (Table 21.1)

21.2 VOC ADDS Mix (Table 21.2)

21.3 VOC Main Mix (Table 21.3)

21.4 VOC LCS Mixture (Table 21.4)

21.5 U.S. Environmental Protection Agency, "Method 8260B Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry", Test methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 2, August, 1996.

21.6 U.S. Environmental Protection Agency, "Method 8000C Determinative Chromatographic Separations", Test methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 3, March, 2003.

21.7 U.S. Environmental Protection Agency, "Method 5030C: Purge and Trap for Aqueous Samples", Revision 3, May, 2003.

21.8 U.S. Environmental Protection Agency, "Method 5035A: Purge and Trap for Aqueous Samples", Draft Revision 1, July 2002.

21.9 ALS Environmental Quality Assurance Manual, Version (most current)

21.10 Appendix I – Procedure for the analysis of 1,4-Dioxane by 8260 SIM method.

Table 21.1 – VOC Gases

Bromomethane	Dichlorodifluoromethane
Chloroethane	Trichlorofluoromethane
Chloromethane	Vinyl Chloride

Table 21.2 – VOC ADDS Mix

acetone	amyl acetate
tert-amyl methyl ether	butyl acetate
tert-butyl alcohol	2-butanone
cyclohexanone	diisopropyl ether
ethyl-*tert*-butyl ether	ethyl acetate
2-hexanone	isopropyl acetate
methyl acetate	methyl *tert*-butyl ether
4-methyl-2-pentanone	propyl acetate
vinyl acetate	

Table 21.3 – VOC Main Mix

acetonitrile	acrolein
acrylonitrile	allyl chloride
benzene	benzyl chloride
bromobenzene	bromochloromethane
bromodichloromethane	bromoform
n-butylbenzene	*sec*-butylbenzene
tert-butylbenzene	carbon disulfide
carbon tetrachloride	chlorobenzene
2-chloroethanol	2-chloroethyl vinyl ether
chloroform	chloroprene
2-chlorotoluene	4-chlorotoluene
cyclohexane	dibromochloromethane
1,2-dibromo-3-chloropropane	1,2-dibromoethane
dibromomethane	1,2-dichlorobenzene
1,3-dichlorobenzene	1,4-dichlorobenzene
cis-1,4-dichloro-2-butene	*trans*-1,4-dichloro-2-butene
1,1-dichloroethane	1,2-dichloroethane
1,1-dichloroethene	*cis*-1,2-dichloroethene
trans-1,2-dichloroethene	1,2-dichloropropane
1,3-dichloropropane	2,2-dichloropropane
1,1-dichloropropene	*cis*-1,3-dichloropropene
trans-1,3-dichloropropene	diethyl ether
1,4-dioxane	ethylbenzene
ethyl methacrylate	heptane
hexachloro-1,3-butadiene	hexachloroethane
hexane	iodomethane
isobutyl alcohol	isopropylbenzene
4-isopropyltoluene	methacrylonitrile
methylcyclohexane	methyl acrylate
methyl methacrylate	methylene chloride
2-methylnaphthalene	naphthalene
nitrobenzene	2-nitropropane
pentachloroethane	propionitrile
n-propylbenzene	styrene
1,1,1,2-tetrachloroethane	1,1,2,2-tetrachloroethane
tetrachloroethene	tetrahydrofuran
toluene	1,2,3-trichlorobenzene
1,2,4-trichlorobenzene	1,3,5-trichlorobenzene
1,1,1-trichloroethane	1,1,2-trichloroethane
trichloroethene	1,2,3-trichloropropane
1,1,2-trichlorotrifluororethane	1,2,3-trimethylbenzene
1,2,4-trimethylbenzene	1,3,5-trimethylbenzene
2,2,4-Trimethylpentane	*m*-xylene
o-xylene	*p*-xylene

Table 21.4 - VOC LCS Mixture

acetone
benzene
bromodichloromethane
2-butanone
chloroacetonitrile
chloroethane
2-chlorotoluene
cis-1,3-dichloropropene
1,2-dibromo-3-chloropropane
dichlorodifluoromethane
1,4-dichlorobenzene
1,1-dichloroethene
1,3-dichloropropane
diethyl ether
ethylbenzene
hexachloroethane
4-isopropyltoluene
methylcyclohexane
methylene chloride
naphthalene
2-nitropropane
propionitrile
tert-amyl methyl ether
1,1,1,2-tetrachloroethane
tetrahydrofuran
trans-1,3-dichloropropene
1,2,4-trichlorobenzene
trichloroethene
1,2,4-trimethylbenzene
vinyl chloride
p-xylene
acrylonitrile
bromobenzene
bromoform
carbon disulfide
chlorobenzene
chloroform
4-chlorotoluene
cyclohexane
1,2-dibromoethane
1,2-dichlorobenzene
1,1-dichloroethane
1,1-dichloro-2-propanone
2,2-dichloropropane
diisopropyl ether
ethyl *tert*-butyl ether
2-hexanone
methacrylonitrile
methyl iodide
4-methyl-2-pentanone
n-butylbenzene
n-propylbenzene
sec-butylbenzene
tert-butyl alcohol
1,1,2,2-tetrachloroethane
toluene
trans-1,4-dichloro-2-butene
1,1,1-trichloroethane
trichlorofluoromethane
1,3,5-trimethylbenzene
m-xylene
allyl chloride
bromochloromethane
bromomethane
carbon tetrachloride
1-chlorobutane
chloromethane
cis-1,2-dichloroethene
dibromochloromethane
dibromomethane
1,3-dichlorobenzene
1,2-dichloroethane
1,2-dichloropropane
1,1-dichloropropene
ethyl methacrylate
hexachlorobutadiene
isopropylbenzene
methyl acrylate
methyl methacrylate
methyl *tert*-butyl ether
nitrobenzene
pentachloroethane
styrene
tert-butylbenzene
tetrachloroethene
trans-1,2-dichloroethene
1,2,3-trichlorobenzene
1,1,2-trichloroethane
1,2,3-trimethylbenzene
1,2,3-trichloropropane
o-xylene

21.10 APPENDIX I – Procedure for the analysis of 1,4-Dioxane by 8260 Selective Ion Monitoring (SIM)

(All sections of this SOP apply unless otherwise specified below)

- Scope and Application –
  - Method 8260 can be used to determine 1,4-Dioxane at a much lower level than a typical scan analysis, by using selective ion monitoring (SIM). Instead of scanning across the entire range of ions, the SIM method only focuses on a few ions so the signal for those ions is much greater. The following compounds may be determined by this method:

Compound name	Primary Ion, Secondary Ions	IS Reference
1,4-Dioxane	96, 62	1,4-Dioxane-d8
Toluene-d8 (Surrogate)	98, 100	1,4-Dioxane-d8
1,4-Dioxane-d8 (IS)	88, 58	

- Instrument Conditions –
  - Oven:
    Initial temp.: 40°C
    Initial time: 4.00 min
    Ramps:

# Rate	Final temp.	Final time
15°C/min	200°C	0.00 min

    Run time: 14.667 min

    Front Inlet:
    Mode: Split
    Initial temp: 200°C
    Pressure: 20.221 psi
    Septum purge flow: 3 mL/min.
    Purge time: 1.00 min.
    Total flow: 55.077 mL/min.
    Gas type: Helium

    Column:
    Restek RXI-624
    Nominal length: 20.0 m
    Nominal diameter: 180.00 um
    Nominal film thickness: 1.00 um

    SIM Parameters:

Group 1 Mass	Dwell
58	50
96	50
62	50
98	50
88	50
100	50

- Procedure:
  - Soil samples are extracted by SW846 method 5035A
  - Water samples are prepared by SW846 method 5030C.

  - 1,4-Dioxane Internal/Surrogate Standard (for Archons adding 1 uL of standard)
    Toluene-d8 (2000 ug/mL) 125 ug/mL
    1,4-Dioxane-d8 (2000 ug/mL) 250 ugL
    Dilute to 5 mL in a volumetric flask with P&T grade methanol.

  - Atomx 1,4-Dioxane Internal/Surrogate Standard (for Atomx's and Centurions adding 5 uL of standard)
    1 mL 1,4-Dioxane Internal/Surrogate Standard
    Dilute to 5 mL in a volumetric flask with P&T grade methanol.

  - Matrix Spike: 1,4-Dioxane (1000 ug/mL Absolute Standards)
    Working spike: 200 uL stock standard diluted to 5 mL with P&T grade methanol
    LCS: 50 uL into 50 mL DI water.
    MS/MSD: For waters: 40 uL into 40 uL of sample.
    For soils: 50 uL into 1 mL methanol extract diluted to 50 mL with DI water.

  - Calibration Standard :
    1,4-Dioxane (2000 ug/mL Restek)
    100 uL standard diluted to 5 mL with P&T grade methanol

  - Refer to section 10.7.15.1 for calibration levels and spike amounts.

- Quality Control
  - The internal standards must meet the requirements in section 11.4.2.4.
  - The accuracy acceptance criteria for soil and waters are ± 20% for the CCV, LCS, MS/MSD, and Surrogates.
  - The precision acceptance criteria (% RPD) for the MS and MSD is 30%.
  - Refer to section 16 for corrective action measures should Quality Contol not meet these criteria.

ALS Standard Operating Procedure

DOCUMENT TITLE:	HERBICIDES
REFERENCED METHOD:	SW8151A
SOP ID:	HS-GCECD003
REV. NUMBER:	08.1
EFFECTIVE DATE:	07/01/2016

ALS Environmental

HERBICIDES

SW8151A

SOPID:	HS-GECD003	Rev. Number:	08.1	Effective Date:	07/01/2016

Approved By: _____ Date: 6-22-16
Semi Supervisor- Kristin Neir

Approved By: _____ Date: 6-22-16
QA Manager - Theodore Yen

Approved By: _____ Date: 06-22-2016
Laboratory Director -Hoai Van

Archival Date:	Doc Control ID#:	Editor:

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
	QA	9-5-17

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HERBICIDES BY SW8151A

1) Scope and Applicability

1.1 Method 8151A is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides and related compounds in aqueous, soil and waste matrices. Specifically the method may be used to determine the following compounds:

Table 1.1 - Chlorinated Herbicides by Method 8151A

Compound	CAS No.	Compound	CAS No.
2,4-D	94-75-7	Dicamba	1918-00-9
2,4-DB	94-82-6	Dichloroprop	120-36-5
2,4,5-TP (Silvex)	93-72-1	Dinoseb	88-85-7
2,4,5-T	93-76-5	MCPA	94-74-6
Dalapon	75-99-0	MCPP	93-65-2

1.2 Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), sample preparation for method describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil. The sample preparation procedures are described in separate SOPs. Refer to Tables in §23 for Limit of Detection (LOD) and Limit of Quantitation (LOQ) for analytes in this method.

2) Summary of Procedure

2.1 This method provides gas chromatographic conditions for the analysis of chlorinated acid herbicides in extracts prepared from water, soil, and waste samples.

2.2 Water samples are extracted with methylene chloride and esterified with diazomethane. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents. For the water extraction procedure, refer to SOP HS-EXT - 003.

2.3 Soil and waste samples are extracted with methylene chloride and esterified with diazomethane. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents. For the soil extraction procedure, refer to SOP HS-EXT - 004.

3) Definitions

3.1 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 **megohms**-cm). For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.17 Confirmation of Positive Results: Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the present of target analytes identified.

3.18 Initial Calibration (ICAL) - Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.

3.19 Initial Calibration Verification (ICV): A known interference free matrix spiked a known concentration of the target analyte. The ICV is prepared from a source different from that used to prepare calibration standards and CCV. This standard is analyzed immediately after the calibration to confirm the usability of the calibration.

3.20 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.21 GC/ECD = Gas Chromatograph / Electron Capture Detector.

3.1 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.2 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.3 Preparation Batch: This is a defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.). For Method 608, the preparation batch size is 10 or less

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible

level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Electron Capture Detectors are sealed by the manufacturer to prevent radiation leakage. ECDs are routinely tested for radiation leakage and serviced only by authorized service providers.

4.6 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due to lifting and placing samples on storage locations and cuts from broken sample containers.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of compressed gasses cylinders.	Suffixation hazard and cylinder fall hazard. Fire hazard when using flammable gas.	Do not used in confined space, ensure proper ventilation and secure cylinders to prevent falls. Ensure all regulators and gas lines are in good repair and do not leak.
Job Task #4:	**Hazards**	**Preventative Measures**

Glassware cleaning	Cuts from broken or chip glassware.	Wear proper gloves, safety glasses and lab coat or apron.
Job Task #5:	**Hazards**	**Preventative Measures**
High temperature Injectors and Detectors.	Burn hazards	Allow detectors and injectors to cool down before performing maintenance.
Job Task #6	**Hazards**	**Preventative Measures**
Handling syringes	Pricking oneself with syringe.	Wear proper gloves, safety glasses, lab coat or apron and handle syringe carefully.
Job Task #7:	**Hazards**	**Preventative Measures**
ECD Detector	Exposure to radioactive ^{63}Ni.	Perform wipe test every six months to check for leaks. Agilent detectors must be checked at three locations, see 4.5 Do not disassemble detector in attempt to repair. Always send detectors to certified repair facility

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 The electron capture detectors measure chlorinated compounds. Exposure of the detectors to extraneous chlorinated sources, such as methylene chloride, must be avoided.

5.3 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Refer to SOP HS-EQ-004.

6) Interferences

6.1 Sources of interference in this method can be grouped into three broad categories.

- 6.1.1 Contaminated solvents, reagents, or sample processing hardware.
- 6.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- 6.1.3 Compounds extracted from the sample matrix to which the detector responds.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

6.3 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

6.4 Use of high purity reagents and solvents helps to minimize interferences.

6.5 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

6.6 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure.

6.7 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of Dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

6.8 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

6.9 To achieve good recoveries, sample extracts should be dried prior to methylation.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality

requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for
- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 All samples must be refrigerated at >0 to 6°C from the time of collection until receipt at the laboratory and while in laboratory storage prior to processing for analysis. Prepared extracts must be stored >0 to 6°C until ready for analysis. Refer to Table 8.1 for sample containers, sample preservation and sample holding time information for sample received.

Table 8.1 Semivolatile Organics / Organochlorine Pesticides / PCBs / Herbicides

TABLE 8.1 – Semivolatile Organics / Organochlorine Pesticides / PCBs / Herbicides			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	125-mL widemouth glass with Teflon lined lid.	Receive cooled to >0 to 6 °C. Store received samples above zero to 6 °C.	Samples extracted within 14 days; extracts analyzed within 40 days after extraction.
Aqueous Samples With No Residual Chlorine Present	2 x 1-L, amber glass container with Teflon-lined lid.	Receive cooled to >0 to 6°C. Store received samples above zero to 6 °C.	Samples extracted within 7 days; extracts analyzed within 40 days after extraction.
Aqueous Samples WITH Residual Chlorine Present	2 x 1-L, amber glass container with Teflon-lined lid.	Add 3-ml 10% sodium thiosulfate solution per gallon (0.008%). Receive cooled to >0 to 6 °C. Store received samples above zero to 6 °C.	Samples extracted within 7 days; extracts analyzed within 40 days after extraction.
Solid Samples (e.g. soils, sediments, sludges, ash)	250-mL widemouth glass container with Teflon-lined lid	Receive cooled to >0 to 6 °C. Store received samples above zero to 6 °C.	Samples extracted within 14 days; extracts analyzed within 40 days after extraction.

9) Equipment and Supplies

9.1 Volumetric flasks, Class A. Various sizes.

9.2 Amber glass vials with Teflon-lined screw tops (or crimp tops), 2-mLs.

9.3 Analytical Balance, capable of measuring to the nearest 0.0001g (0.1mg) - serviced annually and verified daily prior to use.

9.4 Gas chromatograph - A HP 5890 GC, Agilent 6890, Agilent 7890 (or equivalent) equipped with dual ECDs.

9.5 GC columns - The dual column approach involves a single injection split between two columns using a Y-shaped fused silica connector in a single GC. The columns used are:

- 9.5.1 30.0m x 0.53mm ID x 0.50um Rtx-CLPesticides (Restek cat.# 11140) or equivalent
- 9.5.2 30.0m x 0.53mm ID x 0.42 um Rtx-CLPesticides2 (Restek cat.# 11340) or equivalent
- 9.5.3 5m x 0.53mm ID Deactivated Guard Column or equivalent

10) Standards and Reagents

10.1 Note: Store all purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) in glass containers having Teflon™ lined lids. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. Document all preparations in reagent/standard prep logbook and label storage bottles with content, concentration and expiration date. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include n-hexane, methylene chloride, acetone and ethyl acetate must be exchanged to n-hexane prior to analysis. Acetone or toluene may be required for the preparation of some standard solutions. All solvents and chemicals must be pesticide quality or equivalent.

10.3 Methanol, Reagent or Pesticide Grade

10.4 Hexane, Reagent or Pesticide Grade

10.5 All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem. All solvents must be pesticide quality or equivalent. Reagent grade or pesticide grade chemicals shall be used.

10.6 Stock Standards

10.6.1 ICAL and CCV

- 10.6.1.1 AccuStd Methyl Derivatives of Chlorinated Herbicides Mix (Cat. # M-8150)
- 10.6.1.2 2,4 DCAA Methyl Esters - Surrogate (Cat. #M-515-SS)

10.6.2 ICV

- 10.6.2.1 AccuStd EPA Method 8150 Analytes Mix (Cat. #82511)
- 10.6.2.2 MCPA Methyl Derivation (Cat. # 81509)
- 10.6.2.3 MCPP Methyl Derivation (Cat. #81510)
- 10.6.2.4 2,4-DCAA AccuStd (Cat. #M-515-SS)

10.7 Initial Calibration Curve Standards / Continuing Calibration Verification Standard

10.7.1 Intermediate Standard

10.7.1.1 1mL AccuStd Methyl Derivatives of Chlorinated Herbicides
10.7.1.2 1mL 2,4 DCAA Methyl Esters - Surrogate

10.7.2 Level 1 Calibration Standard
10.7.2.1 5 uL Intermediate Standard into 25mL Volumetric. Bring to volume with Hexane.

10.7.3 Level 2 Calibration Standard
10.7.3.1 25 uL Intermediate Standard into 25mL Volumetric. Bring to volume with Hexane.

10.7.4 Level 3 Calibration Standard
10.7.4.1 50 uL Intermediate Standard into 25mL Volumetric Bring to volume with Hexane.

10.7.5 Level 4 Calibration Standard / Continuing Calibration Verification Standard
10.7.5.1 250 uL Intermediate Standard into 50mL Volumetric. Bring to volume with Hexane.

10.7.6 Level 5 Calibration Standard
10.7.6.1 250 uL Intermediate Standard into 25mL Volumetric. Bring to volume with Hexane.

10.7.7 Level 6 Calibration Standard
10.7.7.1 375 uL Intermediate Standard into 25mL Volumetric. Bring to volume with Hexane.

10.7.8 Level 7 Calibration Standard
10.7.8.1 500 uL Intermediate Standard into 25mL Volumetric. Bring to volume with Hexane.

Table 10.6.1 Initial Calibration Standards - Concentration (ng/mL)

Analyte	Level 1	Level 2	Level 3	Level 4 CCV	Level 5	Level 6	Level 7
2,4-D methyl ester	10	50	100	250	500	750	1000
2,4-DB methyl ester	10	50	100	250	500	750	1000
2,4,5-TP methyl ester	10	50	100	250	500	750	1000
2,4,5-T methyl ester	10	50	100	250	500	750	1000
Dalapon methyl ester	10	50	100	250	500	750	1000
Dicamba methyl ester	10	50	100	250	500	750	1000
Dichlorprop methyl ester	10	50	100	250	500	750	1000
Dinoseb methyl ester	10	50	100	250	500	750	1000
MCPA methyl ester	1000	5000	10000	25000	50000	75000	100000
MCPP methyl ester	1000	5000	10000	25000	50000	75000	100000
DCCA (Surr) methyl ester	10	50	100	250	500	750	1000

Table 10.6.2	Calibration Standards - Concentration Conversions for MW.			
Analyte - ester form	MW	Analyte, acid form	MW	Correction Factor
2,4-D methyl ester	235.06	2,4-D	221.05	0.9404
2,4-DB methyl ester	263.12	2,4-DB	249.09	0.9467
2,4,5-TP methyl ester	283.54	2,4,5-TP	269.51	0.9505
2,4,5-T methyl ester	269.51	2,4,5-T	255.48	0.9479
Dalapon methyl ester	157.00	Dalapon	142.97	0.9106
Dicamba methyl ester	235.06	Dicamba	221.04	0.9404
Dichlorprop methyl ester	249.09	Dichlorprop	235.06	0.9437
Dinoseb methyl ester	254.20	Dinoseb	240.21	0.9450

Table 10.6.2	Calibration Standards - Concentration Conversions for MW.			
Analyte - ester form	MW	Analyte, acid form	MW	Correction Factor
MCPA methyl ester	214.65	MCPA	200.62	0.9346
MCPP methyl ester	228.67	MCPP	214.65	0.9387
DCCA (Surr) methyl ester	219.06	DCCA (Surr)	205.45	0.9379

Table 10.6.3	Initial Calibration Standards - Concentration (ug/mL) - Acid Form						
Analyte - Acid Form	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
2,4-D	0.00940	0.04702	0.09404	0.23510	0.47020	0.70530	0.94040
2,4-DB	0.00947	0.04734	0.09467	0.23670	0.47340	0.71000	0.94670
2,4,5-TP	0.00950	0.04753	0.09505	0.23760	0.47530	0.71290	0.95050
2,4,5-T	0.00948	0.04740	0.09479	0.23700	0.47400	0.71090	0.94790
Dalapon	0.00911	0.04553	0.09106	0.22770	0.45530	0.70530	0.91060
Dicamba	0.00940	0.04702	0.09404	0.23510	0.47020	0.70530	0.94040
Dichlorprop	0.00944	0.04719	0.09437	0.23590	0.47190	0.70780	0.94370
Dinoseb	0.00945	0.04725	0.09450	0.23630	0.47250	0.70880	0.94500
MCPA	0.93460	4.67300	9.34600	23.3700	46.7300	70.1000	93.4600
MCPP	0.93870	4.69400	9.38700	23.4700	46.9400	70.4000	93.8700
DCCA (Surr)	0.00938	0.04690	0.09379	0.23450	0.46900	0.70340	0.93790

10.8 Initial Calibration Verification Standard

10.8.1 In a 25 mL Volumetric, add

10.8.1.1 31.25 uL AccuStd EPA Method 8150 Analytes Mix

10.8.1.2 312.5 uL MCPA Methyl Derivation

10.8.1.3 312.5 uL MCPP Methyl Derivation

10.8.1.4 62.5 uL 2,4-DCAA Methyl Ester

10.8.2 Bring to volume with Hexane.

Table 10.7 Initial Calibration Verification Standard - Concentration (ng/mL)

Analyte	ICV
2,4-D methyl ester	250
2,4-DB methyl ester	250
2,4,5-TP methyl ester	250
2,4,5-T methyl ester	250
Dalapon methyl ester	250
Dicamba methyl ester	250
Dichlorprop methyl ester	250
Dinoseb methyl ester	250
MCPA methyl ester	25000
MCPP methyl ester	25000
DCCA (Surr) methyl ester	250

10.9 Transfer the stock standard solutions to vials with PTFE-lined screw caps. Store at or below 6°C, protected from light. Check stock standard solutions frequently for signs of degradation or evaporation.

10.10 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem.

11) Method Calibration

11.1 Operating Conditions for analysis: The dual-column / dual-detector approach involves

the use of two fused-silica open-tubular columns of different polarities, thus, different selectivity towards the target analytes. The columns are connected to an injection tee and separate electron capture detectors. For GC operating conditions, see Table 11.1.

Table 11.1 GC Operating Conditions

Table 11.1 – GC Operating Conditions	
GC Conditions	GC Column Pair – Section 9.2
Carrier gas:	Helium
Carrier gas flow rate:	2.8ml/minute @120°C
Head pressure:	3 psi (constant)
Makeup gas:	Nitrogen
Makeup gas flow rate:	30ml/minute
Injector temperature:	200°C
Detector temperatures:	300°C
Temperature program:	60°c for 1 minute, to 250°C at 9°C/minute, 20oC/min to 300°C then hold for 7.5 minutes.

11.2 Note: Once optimized and calibrated, the same GC conditions must be used for analysis of all standards, samples, blanks and QC samples (LCS/MS/MSD).

11.3 Initial Calibration Curve: External standard calibration is used with Method 8151A because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because of the sensitivity of the electron capture detector, the injection port and column must always be cleaned prior to performing the initial calibration.

- 11.3.1 A standard containing a mixture of esterified acid herbicides is used for initial calibration. A minimum of five concentrations is used to demonstrate the linearity of the detector response. For all Acid Form reporting, the acid form converted concentrations in Table 10.6.3 are used for the ICAL, etc.
- 11.3.2 The peak area is used for quantitation of each component.
- 11.3.3 A 2-µL injection volume of each calibration standard is used. Other injection volumes may be employed, if sensitivity for the compounds of interest is adequate.

11.4 Choosing the Initial Calibration Model: SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data. The analyst will choose the most appropriate model for each analyte. This SOP provides acceptance criteria for initial calibrations using either linear or non-linear models. NOTE: The option for non-linear calibration may be necessary but it may not be used to compensate for detector saturation or to avoid proper instrument maintenance. The calibration model must be continuous and monotonic. The choice of a specific calibration model can be made in one of two ways.

- 11.4.1 The first way is to begin with the simplest approach, the linear model through the origin, and then progress through other options until the calibration acceptance criteria are met.
- 11.4.2 The second way is to use a priori knowledge of the detector response to the target compound to choose the calibration model. Such knowledge may come from previous experience (i.e. knowledge of the typical detector response).

11.5 Evaluation of the Calibration Approach: When any analyte RSD approaches or exceeds 20%, the plotting and visual inspection of a calibration curve should be performed as diagnostic tool to evaluate the curve fit. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the

chromatographic system, analytes that exhibit poor chromatographic behavior, etc. Based upon the inspection of the curve, a first order (linear fit) or second order fit (quadratic) can be evaluated for the calibration. Linear fits require five levels minimally and quadratic fits require six levels minimally. The % Difference as derived from the inspection of the calibration curve should be less than 20% for every analyte and at each level of calibration. This practice for the examination of initial calibration curves is useful when determining the acceptability of the data used to fit the curve.

11.6 Whichever calibration model is selected, the model can be checked to establish the applicability of the model over the extent of the calibration range. This check is performed by re-quantifying the calibration data using the new curve and comparing the calculated concentrations of the calibrations data against the concentration of the calibration level. Using % difference, the criteria for acceptability based upon the additional check demonstrates the impact upon the usability of a calibration for quantitation.

11.6.1 Calculating the % difference is determined by using the following equation:
Where:
% Difference = (Cc – Ce)* 100 / Ce and
Cc = Calculated amount of standard, in mass or concentration units.
Ce = Expected amount of standard, in mass or concentration units.

11.6.2 The absolute value of the % difference between these two amounts for every calibration level should be less than or equal to 20%.

11.6.3 Corrective action may be required if the criteria for %RSD, r, or r2 are not met. If any analyte for any calibration standard has a percent difference with an absolute value greater than 20%, then corrective action may be required. The calibration may not be used for quantitative analyses of that analyte when the %RSD, r, r2, or % Difference criteria are not met.

11.7 For all calibration models the following options are allowed:

11.7.1 Check the instrument operating conditions and perform required maintenance. If any changes to the operating conditions are necessary to achieve linearity for problem compounds, other analyte RSDs may change, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

11.7.2 If the RSD for any analyte is greater than 20% or correlation less the 0.99, the analyst must review the results (proper identification, area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, then that one standard may be reanalyzed once, to rule out problems due to a random chance, and the RSD or correlation recalculated. Replacing the standard may be necessary in some cases. All reanalysis of any calibration standard must be performed within the same 12 shift initiated by analysis of the first ICAL standard. This reanalysis must also commence before any samples are analyzed. If the criteria cannot be met then the entire initial calibration must be performed again.

11.7.2.1 NOTE: Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very

specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

11.7.3 A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the reliable quantitation of the method at low concentration levels. Inquire about regulatory limits or action levels associated with a target analyte adjustment to the lower end of the curve.

11.7.3.1 Replacing one or more of the standards is NOT to be confused with discarding results from a given standard. Replacing a standard requires that the same number of standards, i.e., five or more, be used for calibration.

11.8 Using Calibration Factors (CF) for Initial Calibration

11.8.1 For the initial curve generation, calculate the CF for each analyte at each standard concentration. Calculate the mean CF, and the relative standard deviation (RSD) of the calibration factors. The calculation for the CF and corresponding RSD for each analyte is described in section 15.

11.8.2 If the RSD for each analyte peak is < 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a linear calibration curve or a non-linear calibration model (quadratic) for quantitation.

11.9 For a linear calibration curve ($y = ax + b$), the analyst should not force the line through the origin, but leave the intercept calculated. In addition, do not include the origin (0, 0) as a calibration point. In order to be used for quantitative purposes, a correlation coefficient must be greater than or equal to 0.995.

11.9.1 When the other approaches described above have not met the acceptance criteria, a non-linear calibration model may be employed. The quadratic (second order) model requires six standards.

11.9.1.1 $Y = ax^2+bx+c$

11.9.1.2 For an acceptable non-linear calibration, the coefficient of the determination (COD) must be greater than or equal to 0.99.

11.10 Absolute Retention Time (RT): Establish the absolute retention time for each analyte from the calibration verification standard (CCV) at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. New absolute RTs must be set after installation of a new column. The RTs from the old column may be not be used.

11.10.1 Retention Time Windows: set the RT windows at ± 0.05 min around the center of the absolute RT for each analyte on each chromatographic column and instrument. RT windows are crucial to the identification of target compounds. Use of RT windows allows the instrument to

compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. Analytes are identified when peaks are observed in the compound's RT window on both GC columns. RT window widths should be verified using data from several standards (e.g. CCVs) to create a 72-hour RT study (where RT windows are defined ± 3 times standard deviation for each analyte RT). If the study produces windows that exceed the required width (± 0.05-min), the GC system should be checked and maintenance performed as necessary. Using windows that are too wide may produce false positives. Using windows that are too narrow may produce false negatives.

11.11 Initial Calibration Verification (ICV)

11.11.1 Verify each new Initial Calibration using a second source (ICV) standard at or near the midpoint of the curve. Agreement with the new curve should be ± 20 percent of the true value of the second source standard. An alternate concentration of calibration verification standard should be run periodically to evaluate a different point of the calibration curve.

11.12 Continuing Calibration Verification (CCV)

11.12.1 Verify calibration at the start of each analytical sequence by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected after every ten (10) samples and at the end of the analysis sequence.

11.12.2 The concentration for each analyte must not exceed a ± 20 percent difference from the true concentration. If a linear calibration model or a non-linear model not forced through the origin has been employed for the initial calibration, % drift must be

11.12.3 Although analysis of a single mid-concentration CCV satisfies a minimum CCV requirement, use of a different CCV concentration during analyses is recommended. The occasional use of an alternative CCV concentration evaluates whether the detector response has remained stable for all the analytes over the calibration range.

11.12.4 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

Absolute Retention Time (RT): Establish the absolute retention time for each analyte from the calibration verification standard (CCV) at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. New RTs must be set after installation of a new column. The retention times from the old column may be not be used.

11.12.5 Retention Time Windows: set the retention time windows at ± 0.05 or ± 0.07 min around the center of the absolute retention time for each analyte on each chromatographic column and instrument (see Table 11.12.1). RT windows are crucial to the identification of target compounds. Use of RT windows allows the instrument to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. Analytes are identified when peaks are observed in the compound's RT window on both GC columns. RT window widths must be verified using data from several

standards (e.g. CCVs) to create a 72-hour RT study (where RT windows are defined ± 3 times standard deviation for each analyte RT). If the study produces windows that exceed the required width (± 0.05 or ± 0.07-min), the GC system must be checked and maintenance performed as necessary. Using windows that are too wide may produce false positives. Using windows that are too narrow may produce false negatives. The maximum widths of the retention time windows are listed in Table 11.12.1 and Table 11.12.2 for single and multi-component analytes.

12) Sample Preparation/Analysis

12.1 Extraction and hydrolysis of high concentration waste samples

- 12.1.1 Follow SW-846 Method 3580, Waste Dilution, with the following exceptions:
  - 12.1.1.1 Use methylene chloride as the dilution solvent.
- 12.1.2 LSC / MS Spikes: refer to Table 21.2 and extraction SOPs.

12.2 If sample analysis requires both herbicide esters and acids, then the sample extract must be hydrolyzed, refer to extraction SOPs, HS-EXT-003 (Waters) and HS-EXT-004 (Soils).

12.3 Gas chromatographic analysis of samples: All standards, QC samples and client samples are run with the second column confirmation technique. Inject a 2-µL aliquot of the concentrated sample extract or calibration standard.

12.4 Analysis sequence:

- 12.4.1 Initial Calibration Curve and ICV (second source)
- 12.4.2 or Daily initial CCV
- 12.4.3 Instrument Blank
- 12.4.4 Laboratory Control Sample
- 12.4.5 Laboratory Control Sample Duplicate
- 12.4.6 Method Blank
- 12.4.7 Client samples
- 12.4.8 Matrix Spike
- 12.4.9 Matrix Spike Duplicate
- 12.4.10 Client samples (4 or less)
- 12.4.11 CCV
- 12.4.12 Client samples (10 or less)
- 12.4.13 CCV at end of sequence
- 12.4.14 For dual column confirmation, each compound detected must be present on both columns.

12.5 Dual Column confirmation: Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window for the standard. Each tentative identification must be confirmed using a second GC column of dissimilar stationary phase. When results are confirmed using a second GC column, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. Unless otherwise specified in an approved project plan, the higher result is reported when the RPD agreement between columns is <40%. The calculation for the relative percent difference (RPD) of the results is found in section 15.

- 12.5.1 The calculation for the relative percent difference (RPD) of the results is found in section 15. When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention

times, etc.

12.5.2 If one column result is significantly higher (RPD >40%), review the chromatograms to see if an obvious overlapping peak is causing an erroneously high result on one column. If there is no evidence of chromatographic problems such as co-elution that contributes to the higher result, report the lower result and P flag the data. Caution must be exercised in evaluating a larger peak on one column only. Should it be so large that a coelution cannot be clearly evaluated, report the lower detection (with the P flag) and be prepared to make the chromatograms available so that the data user can understand the matrix cause for the disparity between the columns.

12.5.3 For DoD project, sample results are always reported from the designated primary column unless obvious interference is present in the primary column, the results reported from secondary column and narrate. If RPD is greater than 40% between columns and no interference is present in both columns, report from the primary column and applied P flag and note in case narrative.

12.6 Example calculations for constituent concentration go to section 15.

12.7 Calibration standards must be analyzed in the same manner as the samples (note that standards are already in the ester form). The calculation of concentration given in section 15 is used (external calibration). The calibration is performed using standards made from methyl ester compounds and the calculation of concentration includes a correction for the molecular weight of the methyl ester versus the acid herbicide. If a sample response exceeds the calibration range, dilute the extract and reanalyze.

12.7.1 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) or calibration standards interspersed within the samples, but not to exceed 10 samples between CCVs.

12.7.2 The results from these bracketing standards must meet the calibration verification (CCV) criteria of ±20%. When a CCV standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent a mis-quantitation and possible false negative result, and re-injection of the sample extracts may be required. More frequent analysis of standards will minimize the number of sample extracts that would have to be re-injected if the QC limits are not met for the CCV. However, if the CCV analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit (i.e., >20%), and the analyte was not detected in the samples analyzed during the analytical shift, then the sample extracts do not require reanalysis. In contrast, if an analyte was detected in a sample extract associated with a high CCV, then re-injection is necessary to ensure accurate quantitation. If an analyte is not detected in the sample and the associated CCV is low (below 20% of the expected response), then re-injection is necessary. This is done to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

12.8 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements for both columns. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.9 Use the calibration standards analyzed during the sequence to evaluate retention time

stability. The retention time windows are established using the absolute retention time of each analyte as described previously. Each subsequent injection of a standard during the analytical sequence (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

12.10 If peak detection and identification are prevented due to interferences, further cleanup is likely required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

13) Troubleshooting

13.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

13.2 Possible problems could be standard mixture degradation, column contamination, or active sites in the column or chromatography system.

13.3 A low concentration of herbicide standard injected on a GC/ECD may adsorb when the GC has not been used for several days or more. To prevent this occurrence, prime (or deactivate) the GC column by injecting a standard mixture approximately 10 to 20 times more concentrated than the mid-concentration standard. This procedure may need to be performed prior to beginning an initial calibration.

13.4 Suggested chromatographic system maintenance - When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

13.4.1 Splitter connections - For dual-columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few centimeters (up to 30 cm) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

13.4.2 Metal injector body - Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any foreign material.

13.4.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

13.4.2.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution; rinse the injector body with toluene, methanol, acetone, and then hexane. Reassemble the injector and replace the columns.

13.4.3 Column Changes

13.4.3.1 Whenever column(s) are change, new calibration must be performed. Analysis may begin only after a successful initial calibration and initial verification. Document column type, serial number and return to status in the maintenance logbook.

13.4.4 Other repairs

13.4.4.1 Items such as syringe change, auto sampler tray and gripper and even injection towers do not require initial calibration, but only calibration verification. Document column type, serial number and return to status in the maintenance logbook.

13.4.5 Major Repairs

13.4.5.1 Major repairs such as change in detectors (new or refoiled), detector boards and other major parts not only requires new calibration but also new MDL study. Document repairs, parts replaced serial number and return to status in the maintenance logbook.

14) Data Acquisition

14.1 Data Acquisition:

14.1.1 A sequence is run using Chemstation and automatically processed by Target; Typical Sample Labeling in Chemstation/Target:

14.1.1.1 CCV
14.1.1.2 PLCSW1-071215 (W=water; S= soil)
14.1.1.3 PBLKW1-071215 (071215 = year, month, day)
14.1.1.4 0712040-01A (Sample ID)
14.1.1.5 0712040-01A MS (Matrix Spike)
14.1.1.6 0712040-01A MSD (Matrix Spike Duplicate)

14.1.2 The processed data is reviewed by an analyst using Target.

14.1.3 Target Reviewed results are manually imported to LIMS for reporting

14.1.4 Files to be transferred to LIMS are converted to CSV files using Target.

14.1.5 Data imported into LIMS by use of appropriate test code (8151_W/Samp or 8151_S/Samp, etc).

14.2 LIMS receives the processed "Target" data in its data entry module and links the data to the samples in a specific work order. The QC batch data is also linked to the data. Once the imported data has been transferred into LIMS and all peer review QC validation steps have been completed, project management reviews the data before final reporting.

15) Calculation, and Data Reduction Requirements

15.1 Quantification Calculations

15.2 Calibration Factor (CF) and calibration RSD calculations (Target):

15.2.1 Calibration Factor for each analyte at each concentration, calculate using:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

and

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:
n = the number of standards analyzed

15.2.2 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

15.3 Calculation of Pearson's Product Moment Correlation Coefficient, r

$$r = \frac{n\sum XiYi - \sum Xi \sum Yi}{\sqrt{n(\sum Xi^2 - (\sum Xi)^2}\sqrt{n(\sum Yi^2 - (\sum Yi)^2}}$$

Where:
X = individual values for independent variable
Y = individual values for dependent variable
n = number of pairs of data.

15.4 Calculation of % difference (using the calibration factors):
15.4.1 % Difference = [(CF – mean CF) x 100] / mean CF
where; CF = the calibration factor from the CCV and
mean CF = the mean calibration factor from the initial calibration

15.5 Calculation of % drift (linear and non-linear regression) uses the following formula:
15.5.1 % Drift = [(Calculated conc. - Theoretical conc.) x 100] / Theoretical conc.

15.6 Dual Column Confirmation RPD: When results are confirmed using a second GC column of dissimilar stationary phase, the analyst evaluates the agreement between the quantitative results on both columns once the identification has been confirmed. Unless otherwise specified in an approved project plan, the higher result is reported when the RPD <40% and qualified with a P-Flag. Calculate the relative percent difference of the results using the formula below.

$$RPD = 2 * [R_1 - R_2] * 100 / (R_1 + R_2)$$

Where R_1 and R_2 are the results on the two columns. The difference result for $[R_1-R_2]$ in the equation above is taken as the absolute value of the difference. Therefore, the RPD is always a positive.

15.7 Sample Quantitation using External calibration, aqueous samples:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

Where:
A = Peak Area for the analyte in the sample.
V_t = Total volume of the concentrated extract (µL).
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The

dilution factor is always dimensionless.

$\overline{\overline{CF}}$ = Mean calibration factor from the initial calibration (area/ng).
V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards must be the same. For this method, V_i = 2 µL.
V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

15.8 Sample Quantitation using External calibration, soil / solid samples:

$$\text{Concentration } (\mu\text{g/L} - dry) = \frac{(A_x)(V_t)(D)}{(\overline{\overline{CF}})(V_i)(W_s)(P)}$$

where A_x, V_t, D, $\overline{\overline{CF}}$, and V_i are the same as for aqueous samples, and
W_s = Weight of sample extracted (g).
P = (percent moisture in sample) / 100, or set P = 1 for a wet-weight basis result

15.8.1 The wet weight or dry weight is reported, depending upon the specific application of the data as per client instructions. LIMS performs wet wt/dry wt calculations once percent moisture is entered for a sample.

$$\% \text{ Moisture} = \frac{(\text{"As received" concentration})}{(100 - \% \text{ moisture})} * 100$$

15.9 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.9.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).

$$\%R = \frac{(SSR)}{SA} \times 100$$

SA = Spike Amount Added (mg/L or mg/kg).

15.9.2 % Recovery, %R (for standards and LCS)

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.9.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.